

C L A I M S

1. Clopidogrel hydrobromide in the crystalline Form I characterized by an X-ray
5 diffraction pattern with characteristic interplanar distances d of 4.01; 4.39 and 3.17 Å.
2. Clopidogrel hydrobromide in the crystalline Form I according to claim 1 characterized
by interplanar distances d of 3.12; 6.99; 5.5; 4.29 and 3.65 Å.
- 10 Clopidogrel hydrobromide in the crystalline Form I according to claims 1 or 2
characterized by bands in the infrared spectra at 1743; 1421; 1237, 760 and 728 cm⁻¹.
4. Clopidogrel hydrobromide in the crystalline Form II characterized by an X-ray
diffraction pattern with characteristic interplanar distances d of 4.52; 3.83; 3.48 Å.
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5. Clopidogrel hydrobromide in the crystalline Form II according to claim 4 characterized
by interplanar distances d of 6.38; 2.76 and 3.23 Å.
6. Clopidogrel hydrobromide in the crystalline Form II according to claims 4 or 5
20 characterized by bands in the infrared spectra at 1754; 1436; 1317 and 1223 cm⁻¹.
7. Clopidogrel hydrobromide of Form III, characterized with peaks ascertained by X-ray
diffraction in the following 2θ positions: 7.796 °; 15.380 °; 18.389 °; 19.369 ° and
23.895 °.
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8. A method of preparation of clopidogrel hydrobromide of the crystalline Form I
according to claims 1-3 characterized in that clopidogrel base dissolved in toluene is
precipitated with a concentrated solution of hydrobromic acid.
- 30 9. The method according to claim 8 characterized in that after precipitation, the resulting
oily matter is mixed with toluene for a time necessary for formation of crystal.

10. The method according to claim 8 characterized in that a 48% solution of hydrobromic acid in water is added to a solution of 5 to 15% of the clopidogrel base in toluene, whereas the molar ratio of the clopidogrel base and hydrogen bromide is 1 : 0.9 to 1.5.

5 11. A method of preparation of clopidogrel hydrobromide of the crystalline Form II according to claims 4-6 characterized in that the clopidogrel base is dissolved in an organic solvent and precipitated with a solution of hydrobromic acid in toluene.

10 12. The method according to claim 11 characterized in that precipitation is performed at temperatures 0 to 30 °C and growth crystals occurs at temperatures lower than 10 °C.

15 13. The method according to claim 11 characterized in that a solution of the clopidogrel base having a concentration of 5 to 40 weight % is used and is precipitated with a solution of hydrogen bromide in toluene having a concentration of 5 to 15 weight %, whereas the molar ratio of the clopidogrel base and hydrogen bromide is 1 : 0.9 to 1.1.

20 14. A method of preparation of clopidogrel hydrobromide of crystalline Form II characterized in that clopidogrel base is dissolved in an organic solvent and precipitated with gaseous hydrogen bromide, and, optionally, the resulting clopidogrel hydrobromide is further dissolved and crystallized from a solvent comprising a C₁-C₅ alcohol or a mixture of a C₁-C₅ alcohol with an ether, ester or ketone.

25 15. The method according to claim 14 characterized in that clopidogrel hydrobromide is precipitated from an organic solvent selected from the group of C₆-C₁₂ aromatic hydrocarbons.

30 16. The method according to claim 14 characterized in that precipitation is carried out at a temperature of -15 °C to 30 °C and growth of crystals occurs at a temperature lower than 10 °C.

17. The method according to claim 14 characterized in that a solution of the clopidogrel base having a concentration of 1 to 40 % is used, the molar ratio of the clopidogrel base and hydrogen bromide being 1 : 0.9 to 1.1.

18. The method according to any of claims 14-17, characterized in that gaseous hydrogen bromide is introduced into a solution of the clopidogrel base having a concentration of 15 to 40 %.

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19. The method according to any of claims 14-16 characterized in that gaseous hydrogen bromide is introduced into a solution of the clopidogrel base having a concentration of 1 to 10 %, clopidogrel hydrobromide of Form III thus being precipitated, which is further crystallized from a C₁-C₅ alcohol or a C₁-C₁₅ alcohol in an admixture with an ether, ester or ketone.

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20. The method according to claim 18 characterized in that clopidogrel hydrobromide of Form II is crystallized from a mixture of a C₁-C₅ alcohol and an ether.

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21. The method according to claim 19 characterized in that clopidogrel hydrobromide of Form II is crystallized from a mixture of 2-propanol and methyl *tert*-butyl ether.

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22. Use of clopidogrel hydrobromide of Form III according to claim 7 for the preparation of clopidogrel hydrobromide of Form II, applicable as a pharmaceutical active substance.